AN INVESTIGATION OF A METHOD OF PREPARATION OF BORON TRIFLUORIDE FROM COLEMANITE ($2CaO \cdot 3B_2O_3 \cdot 5H_2O$)

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by

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To Billie Sue

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

AN INVESTIGATION OF A METHOD OF PREPARATION OF BORON TRIFLUORIDE FROM COLEMANITE ($2CaO \cdot 3B_2O_3 \cdot 5H_2O$)

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The colemanite -SO_3-CaF_2 system was studied to determine the effectiveness of the SO_3-CaF_2 mixture in the preparation of a volatile boron compound from colemanite ($2CaO \cdot 3B_2O_3 \cdot 5H_2O$). Reaction parameters were varied throughout the study to determine that concentration, time of heating, and reaction temperature which would yield the maximum amount of boron in the gaseous phase. The volatile boron compound formed was assumed to be boron trifluoride, since this is the only gaseous boron compound known to be formed from the reactants employed and under the conditions imposed. Boron was volatilized from the reaction mixture in yields approaching 50%, and it was suggested that further refinement of the reaction parameters might substantially increase these yields.

The colemanite-sulfuryl fluoride system was studied briefly in an attempt to determine whether SO_2F_2 might have been formed as an intermediate in the reaction. No evidence was obtained which would substantiate this suggestion.

INTRODUCTION

The purpose of this investigation was to examine a possible means of preparation of boron trifluoride from colemanite. The initial investigation involved the use of a fluorite (crude CaF_2)—sulfuric anhydride mixture as a fluorinating agent. Suggestion of a possible intermediate in the reaction prompted the investigation of the use of sulfuryl fluoride as the fluorinating agent.

Boron trifluoride was first prepared by Sir Humphrey Davy in 1808.[1] This early method of preparation centered around the use of boric acid and fluorspar as starting materials. Later improvements in this method of preparation involved the substitution of boric oxide for the boric acid, and the addition of sulfuric acid to the reactants to prevent the volatilization of silicon tetrafluoride and otherwise enhance the reaction.[2]

Modern methods of preparation of boron trifluoride have incorporated numerous refinements which have improved the low yields of the early preparations. However, the use of boric acid or boric oxide as the starting material has persisted and is common to almost all the commercial methods in use today.

Boron occurs in nature as one of several mineral forms, neither of which is the simple oxide or the acid. Therefore, the minerals must be processed to the stage of the oxide or the acid, and this material is then reacted to produce the trifluoride. It is quite reasonable, then, that a direct preparation for boron trifluoride, eliminating the initial processing of the ore to the oxide or the acid, would receive some attention as an improved means of production.

It has been only recently that the coordinating power of boron trifluoride has been realized. BF_3 is the most powerful acceptor molecule known, having a strong tendency to combine with atoms possessing unshared electron pairs to form a coordinate covalent bond. In 1930, J. A. Nieuwland[3] cited the use of boron trifluoride and mercuric oxide as catalysts in the preparation of acetals. Previous references had been made to the use of BF_3 as a catalyst, but this marked the beginning of a great deal of interest in reactions using BF_3 and its derivatives as catalysts. To meet the demand of industry, a method of preparation was developed by C. F. Swinehart[4] which allowed the profitable production of the gas. This method involved the reaction of either borax, boric oxide, or boric acid to form a compound of the type $M_2^I O \cdot 4BF_3$ which is then reacted with three moles of sulfuric acid to yield four moles of boron trifluoride.

A process has been patented in which fluorosulfonic acid is heated with boric oxide or borates to produce BF_3 and sulfuric acid.[5] This process has the advantage of excluding water from the reaction vessel, thus preventing the formation of hydrogen fluoride. A German patent[6] issued in 1931 describes a preparation in which boric oxide, calcium fluoride and sulfuric anhydride react to produce BF_3 and calcium sulfate. Here again, water is essentially excluded from the reaction vessel to prevent formation of HF. In processes using this type of reaction, the calcium sulfate residue is difficult to remove from the reaction vessel and objections to use of this process have resulted.

Other preparations of boron trifluoride involve starting materials other than the oxide or the acid.[7] These involve the decomposition of

fluoborates in the presence of boric oxide and sulfuric acid and the preparation from boron halides and fluorine. These methods do not utilize the initially available boron source (i.e., the minerals found naturally), and therefore they involve some additional costs in production of the necessary starting materials.

This study was suggested as an analogy to the action of calcium fluoride and sulfuric anhydride on phosphate rock (calcium phosphate) to produce hydrofluoric and phosphoric acids.[8]

The present investigation involved a study of the reaction of colemanite, a naturally occurring boron mineral, with calcium fluoride and sulfuric anhydride to produce BF_3. The utilization of the mineral to obtain the trifluoride as the result of one reaction is desirable from the standpoint of cost and convenience. This study involved carrying out the reaction while varying reaction parameters so as to obtain the highest possible yield. Calculation of free energy changes indicate that the reaction is thermodynamically feasible, showing a large, negative value for the free energy change of the reaction. The subsequent use of sulfuryl fluoride as a fluorinating agent resulted from consideration that an intermediate could be formed in the reaction mixture. The result of this investigation thus extended the scope of the study to include the sulfuryl fluoride-colemanite system as well.

During the course of the study, it became necessary to analyze both hydrolyzed gases and solid materials for boron content. The literature shows references to numerous methods of analysis, including the volumetric determination used in this study.[9] Other methods[10] include the distillation of methyl borate (Chapin's method), several photometric

determinations, and a gravimetric determination involving fixation of distilled methyl borate with lime before weighing. Since none of the boron compounds are sufficiently insoluble to effect complete precipitation with the usual reagents, gravimetric determinations are indirect in nature. The photometric determinations[11] are subject to various interferences (such as fluoride ion) and are designed for the analysis of trace quantities of boron. The volumetric determination was chosen for use in this study due to the speed and ease of analysis as compared to the distillation of methyl borate.

The purpose of this study was to determine the feasibility of the preparation of BF_3 by means of the reactions cited earlier. The investigations carried out were intended to give some manner of evidence which would indicate whether BF_3 could be prepared in sufficient yields using these reactions to merit their commercial use.

MATERIALS AND EQUIPMENT

The colemanite used in the experimental work was furnished by the United States Borax Company and was a test sample from a Turkish deposit. Their analysis showed it to be 42.18% B_2O_3, which corresponds to 82.99% purity.

The sulfuric anhydride used was Baker and Adamson Sulfan (stabilized sulfuric anhydride) Code 2377.

The calcium fluoride was Matheson, Coleman and Bell Fluorspar (Native Powder).

The sulfuryl fluoride used as a fluorinating agent was obtained from the Matheson Company and was of 99.5% minimum purity.

The glycerol used to complex the boric acid in the later analyses was Fisher Laboratory Chemical Grade. This material was neutralized to the phenolphthalein end point with sodium hydroxide to prepare it for use as the complexing agent.

The Karl Fischer reagent was obtained from Fisher Scientific Company and was standardized with reagent-grade sodium tartrate. The titer value was 5.80 mg H_2O/ml KF reagent.

All other chemicals used met ACS standards of purity and were used as received from the supplier.

The reaction vessel was a Parr Instrument Company Series 4500 Pressure Reaction Apparatus, with stirrer and heating jacket included. Certain modifications were made on the reactor to ready it for use in this investigation. The silver rupture disk was removed and replaced with one made of gold, since the sulfuric anhydride substantially shortens the life of the silver disk. The stirring assembly was

removed and a Teflon plug was inserted in its place, since the solids in the reactor could not readily be stirred with the assembly as it was designed.

A hot plate was used to heat solutions during analysis, and the reaction residue was dried using both a hot plate and an infrared heat lamp. The colemanite was dried in iron crucibles which were placed in a muffle furnace at 400°C.

Polypropylene tubing was used for all connections to the reaction vessel for introducing the sulfuric anhydride and removing the gaseous products. Polypropylene is not a satisfactory material for use in handling sulfuric anhydride since it immediately turns dark when contacted by the SO_3. However, since no inert tubing was available, short pieces were replaced after each addition of sulfuric anhydride. The gaseous products were hydrolyzed in an alkaline solution contained in polyethylene bottles, and solutions of these hydrolyzed products were stored in polypropylene bottles.

The determination of water by the Karl Fischer method was carried out using a Fisher Titrimeter which was adapted with a sponge rubber gasket to keep the beaker air tight throughout the titration. Methanol was placed in the beaker, titrant was added to an endpoint, and the sample was then placed in the beaker and titrated.

EXPERIMENTAL

Determination and Removal of Water

Since water must be excluded from the reaction vessel to prevent the formation of hydrogen fluoride, it was necessary to dry the reactants and remove the water of hydration from the colemanite. The composition of colemanite ($2CaO \cdot 3B_2O_3 \cdot 5H_2O$) shows five waters of hydration, and the following procedure was carried out in the removal of this water. A weighed sample of the colemanite was placed in an iron crucible and heated in a muffle furnace at 400°C for two hours. Higher temperatures cause copious fuming, presumably from volatilization of boric oxide. Lower temperatures failed to cause any loss in weight upon heating. Upon heating at 400° for two hours, it was found that a 7.2242 g sample lost weight equal to 1.3937 g. Assuming all this loss in weight to be attributed to loss of water, this corresponds to removal of 98.68% of the water of hydration in the sample.

To verify the preceding results, a Karl Fischer determination of water was carried out on the dried samples. A 0.250 g sample of dried colemanite was titrated with Karl Fischer reagent having a titer of 5.80 mg H_2O/ml of KF reagent. The endpoint was reached after 0.05 ml of titrant had been added, indicating that 1.16 milligrams of water were present in each gram of colemanite. This was judged to be sufficient removal of water, and since a higher drying temperature caused extensive fuming of the colemanite, no attempt was made to remove the last traces of water.

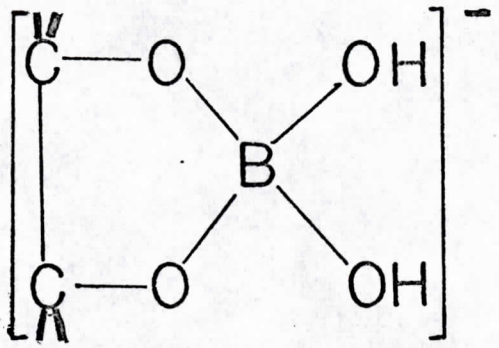
Analysis of the Colemanite

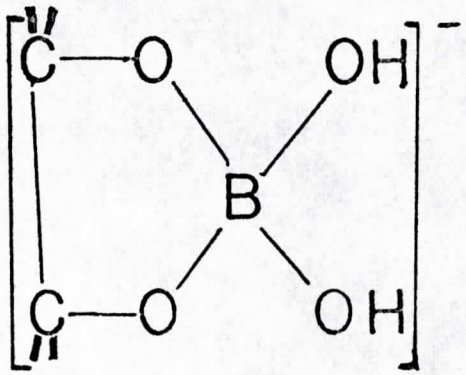
The dried colemanite was then analyzed for boric oxide content. The method used was that of the Pacific Coast Borax Company.[12] The procedure is as follows: The finely ground sample is stirred with 50 ml of water in a beaker and enough concentrated HCl is added to decompose all the borate present. This is boiled until the borate is decomposed and dissolved. The excess acid is neutralized with sodium hydroxide. The solution is made slightly acid to methyl red indicator and a few drops of bromine water are added to oxidize the ferrous iron. After boiling off the excess bromine, about 2 g of finely ground barium carbonate are added, and the solution is boiled for at least two minutes. The volume of the solution at this point should be at least 100 ml for each 0.5 g of B_2O_3 present, to prevent precipitation of barium borate. Excess barium carbonate should be present in the bottom of the beaker at this time.

After boiling, the contents of the beaker are allowed to stand for at least an hour (several, if convenient). The solution is filtered and the residue is washed with water. The filtrate is acidified with HCl, boiled to remove carbon dioxide, and neutralized to the methyl red endpoint with sodium hydroxide. At this point, the boric acid is complexed with mannitol or neutral glycerol as shown in Figure 1 and is titrated with standard sodium hydroxide. The standard alkali is added until the solution becomes pink, and then a drop or two additional is added until the color is a definite reddish-pink, the true endpoint. One milliliter of 1N NaOH is equivalent to 0.03482 g of B_2O_3; the sodium hydroxide used in this investigation was 0.4710N (determined by

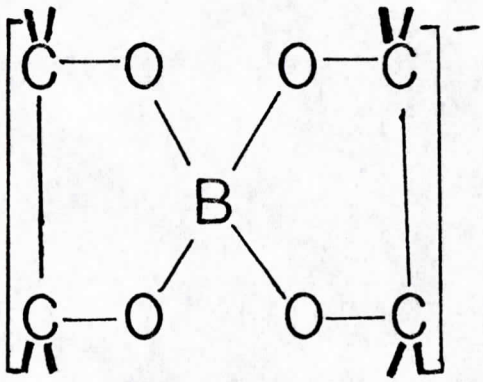
$$B(OH)_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+$$

$$[B(OH)_4]^- + \text{POLYOL} \rightarrow$$





$$+ \text{POLYOL} \rightarrow$$



$$+ H_2O$$

FIGURE 1

THE COMPLEXATION OF BORIC ACID BY POLYOLS

standardization with potassium acid phthalate) and one milliliter is equivalent to 0.01640 g of B_2O_3.

The results of the analysis show that the dried colemanite consists of 55.46% B_2O_3. The precision of the method of analysis is illustrated by examining the results shown in Table I. Three samples were carried through the analysis, giving individual values for the percentage of B_2O_3 as 55.09%, 55.43% and 55.87%, the average of which is 55.46%. The deviation of these values is 0.75% at the maximum, and the purity of the colemanite based on these values is 85.24% as compared to 82.99% purity based on the analysis by U.S. Borax. In light of this agreement, the average values were used in calculations of yields in the reactions carried out.

Experimental Procedure

In the investigation of the action of calcium fluoride and sulfuric anhydride on colemanite, the reactants were placed in the Parr Pressure Reaction Apparatus and allowed to react under various conditions of concentration, temperature and time of reaction. The initial conditions of temperature and time were based on the investigation of the SO_3-CaF_2-phosphate rock system.[13] The initial concentrations were based on calculations from the balanced equation proposed for the reaction:

$$Ca_2B_6O_{11} + 9CaF_2 + 11SO_3 \longrightarrow 6BF_3 + 11CaSO_4$$

For a fifty milliliter (71.7 g) charge of sulfuric anhydride, a stoichiometric ratio of the other reactants would require 56.9 g of calcium fluoride and 31.4 g of dried colemanite.

These conditions were varied in later reactions in an attempt to

TABLE I

ANALYSIS OF THE COLEMANITE USED
IN THE INVESTIGATION

Sample Weight, g	Volume of Titrant, ml	B_2O_3 Present, g	Per Cent B_2O_3	Deviation	Per Cent Deviation
1.5190	48.00	0.8368	55.09	-0.37	0.67
1.5282	48.65	0.8470	55.43	-0.03	0.02
1.3314	42.70	0.7436	55.87	+0.41	0.74
		Average	55.46	±0.27	0.49

determine those conditions of concentration and length of reaction time which would yield the optimum amount of volatile boron compound from the reaction mixture. Table II lists the reactions carried out in this investigation, showing the concentrations of reactants and conditions imposed during each reaction. The temperature was held fairly constant throughout these reactions, being in the range of $250^{\circ} \pm 25^{\circ}C$.

The reactions were carried out in the following manner: Weighed amounts of dried colemanite and dried calcium fluoride were mixed thoroughly in a small bottle and then transferred to the bottom of the reaction vessel. The pressure head was secured in place and a vacuum was carefully pulled on the vessel. A 250 ml separatory funnel was attached to one of the fittings on the pressure head using a short length of polypropylene tubing as shown in Figure 2. The sulfuric anhydride was poured into the separatory funnel, and upon opening the valve to the reaction vessel, the SO_3 was pulled inside. The amount of SO_3 used was first determined as an approximate volume by filling the separatory funnel to a calibrated mark. This was found to be unsatisfactory, and the later determinations were obtained by weighing the stock SO_3 container before and after pouring out the desired amount. The operations involved in charging the reactor and carrying out the reactions were performed under a hood. Once the charge was placed in the reactor, the heater was turned on and the temperature was brought to the desired value.

An iron-constantan thermocouple was employed to determine the temperature of the reactor. Silicone grease was placed in the thermowell of the reactor and as the temperature rose inside the vessel the silicone grease melted. The thermocouple was immersed in the melted grease and

TABLE II

CONDITIONS IMPOSED ON REACTIONS INVOLVING THE COLEMANITE -CaF_2-SO_3 SYSTEM

Reaction Number	Concentration, g			Time of Heating, hr.	Temperature °C
	Colemanite	CaF_2	SO_3		
1	20.000	60.000	50 ml	2	250
2	30.000	60.000	50 ml	2	250
3	33.000	60.000	50 ml	2	250
4	28.662	62.940	50 ml	2	250
5	37.616	85.917	25 ml	2	250
6	30.000	65.000	88.57	2	250
7	30.000	65.000	97.15	15	250
8	27.242	65.000	148.65	2	250
9	30.013	60.000	45.18	2	250
10	30.000	65.000	73.26	2	250

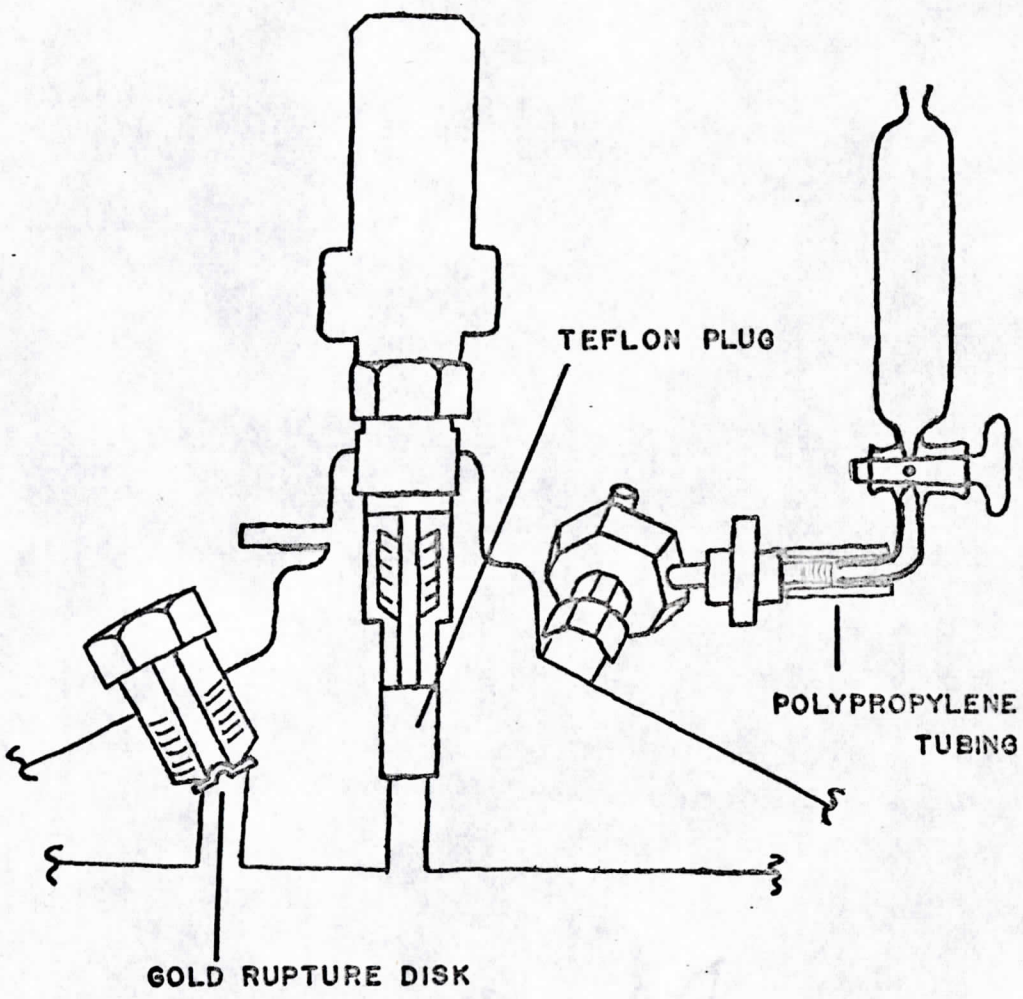


FIGURE 2. PRESSURE HEAD SHOWING ATTACHED SEPARATORY FUNNEL AND OTHER MODIFICATIONS

(NOT TO SCALE)

the leads were connected to a voltmeter calibrated in degrees Centigrade. The temperature was thus read directly from the scale. The heater settings and time of heating to temperature were recorded, and the thermocouple was not used after it was determined that the rate of heating was reproducible.

The reactants were heated for the time desired and were then allowed to cool. At this time, the gaseous products were bled from the reactor and were hydrolyzed with sodium hydroxide solution. Hydrolysis of the gases was accomplished by means of a series of three one-quart polyethylene bottles connected as a scrubbing train to ensure adequate contact of the gases with the liquid. When the internal pressure had dropped, nitrogen was used to sweep the reaction vessel for a period of at least three hours to remove all traces of gaseous products. The volume of the solution was then measured and the material was stored for later analysis.

After sweeping with nitrogen the reaction vessel was opened; the residue material was found to loosen from the vessel quite readily when wet thoroughly with strong sodium hydroxide. This slurry was removed and evaporated to dryness using a hotplate and an infrared heat lamp. Once dry, the material was weighed to determine the total mass of the dry residue. It was transferred to a large mortar and pestle and ground to a very fine consistency to ready the material for analysis.

Reactions Utilizing the SO_3-CaF_2 Mixture

The first and second reactions were carried out with the purpose of checking out the apparatus and determining qualitatively whether any boron was present in the gas phase after reaction. The charge for the first reaction contained less than a stoichiometric amount of colemanite, and the charge for the second contained approximately the required stoichiometric amount. The reaction was carried out according to the procedure outlined, and the hydrolyzed gases were analyzed qualitatively for boron content. This qualitative test consisted of placing 25 ml of the liquid in a porcelain evaporating dish, adding 5 ml of concentrated sulfuric acid and 10 ml of methanol, and igniting the mixture. If boron is present, the volatile methyl borate will be formed and a green flame will be observed immediately. Barium and copper do not interfere since their salts, if present, will not be volatilized immediately. In testing the solutions from the first two reactions, no positive test was observed for the first, whereas the second solution yielded a definite green flame immediately, indicating the presence of boron in the gaseous phase of the reaction products.

Beginning with the third reaction, an attempt was made to quantitatively analyze the hydrolyzed gases and the residue for boron content. The third charge, containing an approximate stoichiometric amount of each reactant, was held at 250°C for two hours, cooled, and the gases removed. The solution containing the hydrolyzed gases was analyzed for boron according to the method cited earlier, with results indicating that 21.0% of the boron in the original charge had been volatilized. No analysis was carried out on the residue for this reaction.

The charge for the fourth reaction contained approximate stoichiometric amounts of reactants, and was conducted in the manner outlined. It was decided that a materials balance should be sought, analyzing both hydrolyzed gases and residue for boron content. The analysis of the hydrolyzed gases showed that 24.3% of the boron had been volatilized, and the residue revealed 22.7% of the boron from the original charge. Thus 47.0% of the boron started with was accounted for after the reaction.

The fifth reaction was carried out with approximately one-half the required stoichiometric amount of sulfuric anhydride, with all other conditions being as stated before. The analysis indicated that 87.6% of the boron remained in the residue while 7.3% was volatilized. Since 94.9% of the boron was accounted for in this analysis, with some 85% in the residue, it was decided that there must have been some loss of gases while bleeding off the volatile products. This could explain the low percentage of boron accounted for in the fourth reaction.

A length of 3/8 inch copper tubing was attached with a compression fitting to the gas outlet on the reactor head. Polypropylene tubing was slipped over the copper tubing and then secured with wire to ensure a gas tight fitting.

The sixth reaction, approximately duplicating the third and fourth in conditions and concentration, indicated that there probably was little if any loss of gases. Although 78.5% of the boron was accounted for, only 21.6% was found in the hydrolyzed gases while 56.9% was present in the residue.

The seventh charge contained approximately one third more than the

required stoichiometric amount of sulfuric anhydride, and the length of time at the reaction temperature was increased to fifteen hours. A slightly higher yield of boron in the gas phase was obtained (28.6%), while 87.7% of the boron in the charge was accounted for.

The eighth reaction was carried out with twice the stoichiometric amount of sulfuric anhydride, holding other conditions as in previous reactions. Since a slight excess of SO_3 in the previous reaction had increased the yield of volatile boron compound, it was suspected that some intermediate product might be formed which was then acting as the fluorinating agent in the reaction. If this were so, an increased amount of SO_3 should enhance the formation of this intermediate, ultimately increasing the yield of boron in the gas phase. This attempt to establish some credence for an intermediate was not successful, however. The analyses for both the hydrolyzed gases and the residue were characterized by a complete absence of precision, and the only conclusion which could be drawn was that some species which interfered with the analysis was present as a result of the excess SO_3.

The ninth reaction, containing two thirds the required stoichiometric amount of SO_3, was carried out under ordinary conditions. The low yield (5.4%) of volatile boron compound tended to verify the results of the fifth reaction, indicating further that the amount of SO_3 present is quite critical as to the amount of volatile boron compound obtained.

The tenth reaction was carried out with the intention of establishing the stoichiometric amount of SO_3 as the most desirable concentration. The other conditions of the reaction were held at their usual values. The yield of boron in the gaseous phase is indicative that the

stoichiometric amount is perhaps the most desirable.

Reactions Utilizing Sulfuryl Fluoride

Since the seventh and eighth reactions had caused some speculation concerning the formation of some intermediate during the process of reaction, it was decided that an investigation should be made concerning this possibility. A search of the literature revealed a patented process[14] in which CaF_2 and SO_3 are reacted under heat and pressure to form sulfuryl fluoride (SO_2F_2) in yields exceeding 98%. Although the temperatures cited in this process were higher than those used in this investigation, it seemed reasonable to investigate the possibility of formation of this material. If sulfuryl fluoride was formed, and if this compound did act as the fluorinating agent, then the addition of SO_2F_2 to the reaction vessel, in the presence of colemanite only, should yield boron in the gaseous phase of the products.

In carrying out the reactions with sulfuryl fluoride it was necessary to devise a method of introducing the gas into the system. No means of measuring the amount of SO_2F_2 transferred was available, and therefore an estimate was made as to the amount introduced into the reactor, with the actual weight of the gas transferred being determined by difference in weight of the container. This method is not desirable, since no control is maintained over the transfer process, and it is practically impossible to transfer a given amount of gas by this method. This objection is readily illustrated by the large (almost four-fold) excess of SO_2F_2 contained in the charge for the eleventh reaction.

The sulfuryl fluoride was transferred to the reaction vessel by

cooling the evacuated vessel overnight in an ice bath and then for four hours in dry ice, lowering the temperature of the vessel below the boiling point of the SO_2F_2. The lecture bottle of gas was attached to the vessel using polypropylene tubing. This connection was evacuated, and the gas was allowed to expand into the reactor and condense there.

The conditions imposed in the reactions using sulfuryl fluoride are summarized in Table III. The eleventh reaction (the first using SO_2F_2) was carried out with a charge containing 30.000 g of dried colemanite and 272.14 g of SO_2F_2. Although this large excess of SO_2F_2 caused some changes in the conditions of the reaction, the reaction was carried out as planned with the usual time of heating and temperature employed. The presence of boron in the gaseous products would indicate the effectiveness of sulfuryl fluoride as a fluorinating agent for this system.

The reaction was carried out with heating for two hours at 250°C, with the pressure rising to 550 psig. After cooling overnight, the gases were bled off and hydrolyzed in strong alkali using the apparatus described earlier. The residue appeared to be completely dry and free of encrustation, being easily removed from the reactor. Analysis of the hydrolyzed gases indicated that 70.7% of the boron in the charge had been volatilized, and the residue analysis indicated that 72.0% of the original boron remained in the residue. Extensive variation of results in the analysis of the residue causes this figure to be highly questionable, and the results of the twelfth reaction cause considerable doubt as to the validity of the analysis of the hydrolyzed gases. As with the seventh and eighth reactions, some species which interferes with

TABLE III

CONDITIONS IMPOSED ON REACTIONS
USING SULFURYL FLUORIDE

Reaction Number	Concentration, g		Preliminary Standing Time, hr.	Time of Heating, hr.	Temperature °C
	Colemanite	SO_2F_2			
11	30.000	272.14	30	2	250
12	55.150	60.53	20	2	250

the boron analysis apparently is formed.

The charge for the twelfth reaction contained 55.150 g of dried colemanite and 60.53 g of sulfuryl fluoride. The SO_2F_2 was introduced into the reactor by the method cited earlier, and the reaction was carried out with heating at 250°C for two hours. After cooling overnight, the gases were collected and both the hydrolyzed gases and the residue were analyzed for boron content.

Analysis of the hydrolyzed gases showed that no boron was present in the gaseous phase, and analysis of the residue indicated that 75.4% of the boron in the original charge remained in the residue. The absence of boron in the gaseous phase indicates that sulfuryl fluoride is not effective as a fluorinating agent under the conditions imposed in this reaction.

DISCUSSION OF RESULTS

In this investigation the action of a CaF_2-SO_3 mixture on colemanite was studied to determine whether a volatile boron compound (presumably the trifluoride) could be prepared using this system. Preliminary investigations showed that a balanced equation could be written for the proposed reaction, and that such a reaction would be thermodynamically feasible due to the large, negative value of the free energy change for the reaction. Ten reactions were carried out with the intention of establishing whether a volatile boron compound would be formed, and if so, how best to adjust the reaction parameters so as to obtain maximum yields of boron in the gaseous phase.

The gaseous products (and unreacted gaseous reactants) were hydrolyzed in strong alkali and the solid residue was collected, dried and ground in a mortar and pestle. Both the residue and the hydrolyzed gaseous products were analyzed for boron content, with an attempt being made to establish a materials balance on the boron in the charge and that recovered in the reaction products. The results of the analyses of the reaction products for the colemanite -SO_3-CaF_2 system are shown in Table IV. The amount of boron in the charge is listed for comparison with the amount accounted for. Listings of amounts of boron are in terms of the oxide (B_2O_3) since this is the usual manner of reporting boron content.[15]

The Colemanite -SO_3-CaF_2 System

The first two reactions were strictly qualitative, with tests being carried out on the hydrolyzed gases for the presence of boron.

TABLE IV

THE COLEMANITE -CaF_2-SO_3 SYSTEM: ANALYSIS OF REACTION PRODUCTS

Reaction Number	B_2O_3 Present					B_2O_3	
	Charge,	Hydrolyzed gases,		Residue,		Accounted for,	
	g	g	%	g	%	g	%
1	11.092	None	-	-	-	-	-
2	16.638	Positive Test		-	-	-	-
3	18.302	3.843	21.0	-	-	-	-
4	15.896	3.847	24.2	3.608	22.7	7.455	46.9
5	20.862	1.523	7.3	18.275	87.6	19.798	94.9
6	16.638	3.594	21.6	9.467	65.9	13.061	78.5
7	16.638	4.758	28.6	9.833	59.1	14.591	87.7
8	15.108	3.656	24.2	9.412	62.3	13.068	86.5
9	16.645	0.982	5.9	10.370	62.3	11.352	68.2
10	16.638	8.086	48.6	0.632	3.8	8.718	52.4

The first reaction, containing a small amount of colemanite, yielded no boron in the gaseous phase, but analysis of the hydrolyzed gases from the second reaction showed a positive test for boron.

The third reaction also yielded boron in the gaseous phase, and a determination of the amount of boron present showed that 21.0% of the boron in the charge had been volatilized. No analysis was carried out on the residue, and a materials balance was not obtained for this reaction.

Since the second and third reactions contained approximate stoichiometric amounts of B_2O_3 in their charges (16.6380 g and 18.3018 g respectively) as opposed to the smaller amount in the first charge (11.0920 g), it was assumed that the stoichiometry of the proposed overall reaction must be adhered to in order to volatilize boron from the colemanite. The fact that in the first reaction the surface of the reaction vessel was as yet untouched by the SO_3-CaF_2 mixture must also be considered, since reaction of this mixture with the surface could have occurred preferentially to the fluorination of the boron.

This first series of reactions served to establish the fact that boron is volatilized from colemanite in the presence of the CaF_2-SO_3 mixture under the reaction conditions, and subsequent reactions were carried out in an attempt to refine the process so as to achieve the maximum yield of boron in the gaseous phase.

The fourth reaction was carried out under the normal reaction conditions, having a stoichiometric ratio of reactants and being heated at 250°C for two hours. The analysis of the residue and the hydrolyzed gases marked the first attempt at obtaining a materials balance on the boron present. The attempt to account for all the boron introduced in

charge was unsuccessful, with only 47.0% being accounted for. A greater yield of boron in the gaseous phase (24.2%) was found, but over 50% of the boron appeared to have been lost at some point in the course of the procedure.

Since boric acid is volatile with steam from strongly acid solutions, it was thought that some loss might have occurred during drying of the residue. However, Feldman[16] reports that the volatilization from acid solution is less than 3% until 90-95% of the solution has been evaporated, and Kostrikin and Korovin[17] found that the loss upon evaporation is negligible from water solutions when evaporation is carried out under "normal analytical conditions". Since the residue was taken up in strongly alkaline solution, and since the drying operations were carried out with the solution remaining strongly basic, it was unlikely that any appreciable loss of boron occurred during this process.

Losses could also have occurred while the gases were being bled from the reactor, since the connection to the reactor may not have been gas tight. This situation was improved in later operations by installation of the gas-tight connection previously described.

The fifth reaction charge contained a slight excess of B_2O_3 (as colemanite) and approximately one-half the required stoichiometric amount of SO_3. This was allowed to react at 250°C for two hours, and the analysis revealed that only 7.3% of the boron in the charge was volatilized under these conditions. Since 87.6% of the boron was found in the residue and only 5.1% was lost during the reaction, it was indicated that a stoichiometric amount of SO_3 is necessary for effective

volatilization of boron by this reaction.

The large percentage of boron in the residue tends to support the conclusion that little if any borate is volatilized during the evaporation and drying of the residue, since the drying process was carried out with the same procedure as had been followed previously.

The sixth reaction was carried out with a slight excess of SO_3 to determine if more than a stoichiometric amount would improve the yield of boron in the gaseous phase. The analysis indicated that the yield was substantially improved over the fifth reaction (with one-half the stoichiometric amount), but the yield of volatile boron compound was slightly less than that obtained using the stoichiometric amount of SO_3. Once again, loss of boron was sustained at some point in the procedure, with 78.5% being accounted for after the reaction.

The time of heating was increased to fifteen hours in the seventh experiment to determine the effect of a longer reaction time. A slight excess of SO_3 was included in the charge for the reaction. Analysis showed that 28.6% of the boron was volatilized under these conditions, indicating that the reaction is only slightly more efficient at longer reaction times. The loss of boron in this reaction was 12.3% as compared to 21.6% in the previous reaction, suggesting that the material lost may have been part of the gaseous phase rather than the residue since most of the increase was in this category.

Due to the fact that a slight excess of SO_3 tended to yield a greater amount of volatile boron compound when reacted for a longer period of time, the effect of a two-fold excess of SO_3 was investigated in the eighth reaction. This was reacted for two hours at 250°C, and

the analysis suggested that the yield of boron was enhanced by this excess. However, the analysis of both the hydrolyzed gases and the residue was questioned due to the very poor precision obtained in the determinations. The hydrolyzed gases were analyzed nine times, with identical 100 ml samples showing values ranging from 15.4% to 38.1%. The residue analysis also showed a wide range of variation with six samples yielding values from 48.8% to 75.3%.

Since the method of analysis used showed good accuracy and precision with known samples (Table I) and since the previous analyses had exhibited good precision, it was evident that some interfering species was present in both the residue and the gaseous phase when a large excess of SO_3 was used. This species was evidently not present except when this large excess was used, and this suggested that some intermediate might be formed in the reaction. Reactions were carried out at a later date to determine whether sulfuryl fluoride might be the species formed.

The ninth reaction was carried out with conditions duplicating those used in the fifth reaction, and the results show that very little boron is volatilized when the SO_3 concentration is significantly lowered. Therefore, the conditions which appeared to be necessary for effective volatilization of boron were a stoichiometric amount of both colemanite and sulfuric anhydride, and heating for at least two hours at 250°C.

These conditions were used in the tenth reaction, and the results of the analysis showed a significantly higher yield of volatile boron compound. This yield of 48.6% of the boron in the gas phase was the

most effective volatilization of boron obtained in any of the reactions attempted with the colemanite -SO_3-CaF_2 system, and it was concluded that the reactants must be present in the indicated ratio for optimum yield to be obtained.

The investigation of the colemanite -SO_3-CaF_2 system thus showed that a volatile boron compound is formed when the reaction is carried out at 250°C for at least two hours, and that the optimum ratio of reactants appears to be the stoichiometric ratio, based on the proposed overall equation for the reaction.

The volatile boron compound was assumed to be boron trifluoride, since this is the only volatile boron compound known to form under these conditions and from these reactants. However, equipment which could be used to identify the gaseous products was not available for this investigation, and as a result no positive identification of the compounds in the gaseous phase could be made. This not only prevented the identification of the boron species, but prevented identification of the species interfering with the boron analysis as well.

The Colemanite -SO_2F_2 System

It was noted in the discussion of the eighth reaction that the presence of some undetermined species prevented a reputable analysis of both the residue and the hydrolyzed gases. The possibility of formation of sulfuryl fluoride as an intermediate in the reaction was noted, and two reactions were carried out with colemanite and SO_2F_2 in the initial charge. The analyses of the products of these reactions are shown in Table V.

TABLE V

THE COLEMANITE-SULFURYL FLUORIDE SYSTEM:
ANALYSIS OF REACTION PRODUCTS

Reaction Number	B_2O_3 Present					B_2O_3 Accounted for,	
	Charge, g	Hydrolyzed gases, g	%	Residue, g	%	g	%
11	16.638	11.763	70.7	11.979	72.0	-	-
12	30.570	0.000	0.0	23.050	75.4	23.050	75.4

The analysis of the eleventh reaction indicated that 70.7% of the boron was volatilized and the residue was shown to contain 72.0% of the original boron. Because the total amount of boron accounted for was obviously incorrect, and because the analysis of the residue showed very poor precision, no conclusion could be reached as to the effectiveness of the SO_2F_2 as a fluorinating agent in this reaction. However, an interesting parallel may be drawn to the situation encountered in the eighth reaction, in which the analysis was characterized by a similar lack of precision. The eighth reaction charge contained a large excess of SO_3, and it was suspected at that point that the formation of some intermediate species was the cause of the extremely poor results obtained in analysis. If SO_2F_2 was formed in the eighth reaction and subsequently caused the interference in the analysis, then the results obtained in the analysis of the products of the eleventh reaction would be as expected, with the excess of SO_2F_2 interfering with the analysis and causing the poor precision and accuracy. It must be pointed out, however, that no experimental evidence was obtained which confirmed the presence of SO_2F_2 in the products of the eighth reaction, and for this reason no conclusion may be drawn at this time.

The twelfth reaction, utilizing a charge consisting of 55.15 g of colemanite and 60.53 g of SO_2F_2, showed no boron in the gaseous phase and 75.4% of the boron remaining in the charge. These results indicated that SO_2F_2 was not effective as a fluorinating agent for boron and that the analysis for the hydrolyzed gases of the eleventh reaction was probably incorrect. Although a much smaller amount of volatile boron compound would be expected with the smaller amount of SO_2F_2 involved in

the previous one, some would be expected to form. Since no boron was found in the gaseous phase, the high value obtained in the analysis of the eleventh reaction was credited to interference by some species present. Due to the large excess present, SO_2F_2 possibly was the interfering species.

The mechanism involved in the formation of a volatile boron compound from the colemanite $-SO_3-CaF_2$ system is not understood at this time, and results of the investigations outlined here indicate that further refinements will be necessary in order to identify the route followed in the formation of this compound. This study showed that the compound was formed in yields up to 48% under the conditions employed, and it is probable that further adjustment of reaction parameters could increase the yields significantly.

SUMMARY AND CONCLUSIONS

The colemanite -SO_3-CaF_2 system was studied to determine the effectiveness of the SO_3-CaF_2 mixture in the preparation of a volatile boron compound from colemanite. Ten reactions were carried out, with the reaction parameters being varied so as to determine those conditions which produce optimum yield of boron in the gaseous phase of the products. It appeared that the stoichiometric ratio was the most efficient concentration of reactants, with these values being determined from the proposed overall reaction:

$$2CaO \cdot 3B_2O_3 + 11SO_3 + 9CaF_2 \longrightarrow 6BF_3 + 11CaSO_4$$

Although the mechanism of the reaction is not known at this time, experiment has shown that a reaction yielding a volatile boron compound does occur. Yields of boron in the gaseous phase amounted to as much as 48.6% of the B_2O_3 in the charge when the stoichiometric ratio of reaction mixture was allowed to react at 250°C for two hours, with lesser amounts of boron being recovered under other conditions.

The presence of some species which interfered in the titration of boric acid was observed in those reactions utilizing excess amounts of SO_3. The possibility that this might be an intermediate in the reaction caused some speculation as to the nature of this compound. Since sulfuryl fluoride may be prepared from a SO_3-CaF_2 mixture under heat and pressure, it was thought that this compound might be formed as the intermediate. Therefore, the colemanite -SO_2F_2 system was briefly examined, with no conclusive evidence being obtained for the possibility of formation of SO_2F_2. Colemanite -SO_2F_2 mixtures of different ratios

were reacted to determine whether a volatile boron compound was formed; an excess of SO_2F_2 appeared to yield a large amount of boron in the gas phase, whereas an excess of colemanite yielded no volatile compound. Since an interfering species was present during the analysis for boron, the validity of the high yield with excess SO_2F_2 was questioned.

Since no equipment was available with which to identify the gaseous compounds, it could not be determined whether the volatile boron compound formed was actually boron trifluoride . It was assumed that this was the compound formed since BF_3 is the only volatile compound of boron known to be formed from these reactants under these conditions. Also, this lack of equipment prevented the resolution of the question concerning the formation of SO_2F_2 in the reaction, since a spectroscopic analysis of the gaseous phase would have determined whether this compound was present.

It may be concluded from the data obtained in the investigation that a volatile boron compound is formed from the reaction, and that the proper choice of reaction parameters can increase the yield of this compound to at least 48%. It is reasonable to assume that further refinement of these parameters might result in an increased efficiency of the SO_3-CaF_2 mixture in volatilizing boron from colemanite.

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